



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :

H01M 10/04, 6/46

A1

(11) International Publication Number:

WO 97/31400

(43) International Publication Date:

28 August 1997 (28.08.97)

(21) International Application Number: PCT/US97/02305

(22) International Filing Date: 20 February 1997 (20.02.97)

## (30) Priority Data:

08/603,894	22 February 1996 (22.02.96)	US
08/630,983	12 April 1996 (12.04.96)	US
08/630,985	12 April 1996 (12.04.96)	US

(71) Applicant (for all designated States except US): VALENCE TECHNOLOGY, INC. [US/US]; 301 Conestoga Way, Henderson, NV 89015 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): VELASQUEZ, David, A. [US/US]; 1881 Desert Forest, Henderson, NV 89012 (US). HOLMES, Douglas, B. [US/US]; 4 John Wilson Lane, Lexington, MA 02173-6033 (US). GOGOLIN, E., Lawrence [US/US]; 26 Whispering Pine Road, Sudbury, MA 01776 (US).

(74) Agent: KREBS, Robert, E.; Burns, Doane, Swecker &amp; Mathis, L.L.P., P.O. Box 1404, Alexandria, VA 22313-1404 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

## Published

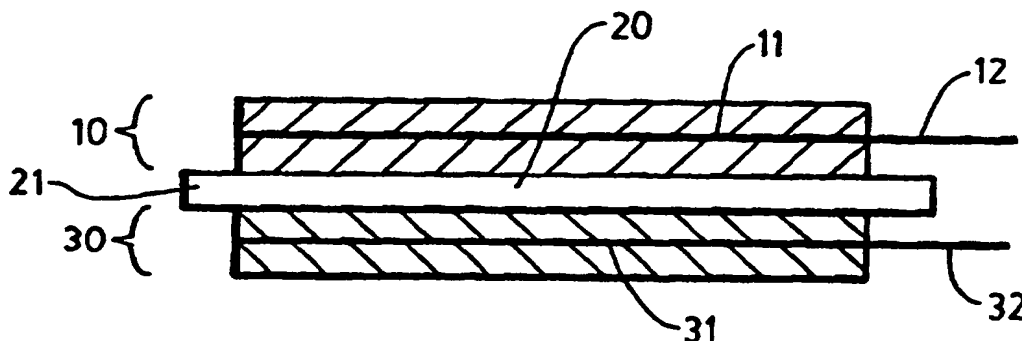
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD AND APPARATUS FOR PREPARING ELECTROCHEMICAL CELLS

## (57) Abstract

A method of fabricating electrochemical cells and batteries wherein the successive anode and cathode layers are separated by a polymeric electrolyte layer having a protruding polymer edge around its perimeter which reduces the likelihood of inadvertent contact between the anode and cathode current collectors is provided. The polymer edge functions as a non-conducting physical barrier positioned between adjacent current collectors. An apparatus for preparing electrochemical cells is also disclosed.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## METHOD AND APPARATUS FOR PREPARING ELECTROCHEMICAL CELLS

### Field of the Invention

The present invention relates to electrochemical devices and, more particularly, to a method of fabricating solid, non-aqueous electrochemical cells demonstrating improved performance.

### BACKGROUND OF THE INVENTION

Non-aqueous lithium electrochemical cells typically include an anode, a lithium electrolyte prepared from a lithium salt dissolved in one or more organic solvents and a cathode of an electrochemically active material, typically a chalcogenide of a transition metal. During discharge, lithium ions from the anode pass through the liquid electrolyte to the electrochemically active material of the cathode where the ions are taken up with the simultaneous release of electrical energy. During charging, the flow of ions is reversed so that lithium ions pass from the electrochemically active cathode material through the electrolyte and are plated back onto the lithium anode.

Recently, the lithium metal anode has been replaced with a carbon anode such as coke or graphite intercalated with lithium ions to form  $\text{Li}_x\text{C}$ . In operation of the cell, lithium passes from the carbon through the electrolyte to the cathode where it is taken up just as in a cell with a metallic lithium anode. During recharge, the lithium is transferred back to the anode where it reintercalates into the carbon. Because no metallic lithium is present in the cell, melting of the anode does not occur even under abuse conditions. Also, because lithium is reincorporated into the anode by intercalation rather than by plating, dendritic and spongy lithium growth does not occur. Non-aqueous lithium electrochemical cells are discussed in U.S. Patent Nos. 4,472,487, 4,668,595 and 5,028,500.

Despite these advantages, present methods of fabricating electrochemical cells produce cells and batteries that are prone to short circuits. This occurs, for instance, when a current collector develops burrs or rough edges during fabrication. These burrs can come into contact with another current collector.

5 Simply reducing the size of the current collectors is not a desirable option of avoiding short circuits as this also reduces the electrical contact area between the current collector and electrode material. In addition, this technique may be difficult to implement with present methods of fabricating electrochemical cells. For instance, where electrochemical cells (or precursors thereof) are mass

10 produced (e.g., cut to size) from a web comprising a tri-layer laminate having (1) an anode layer, (2) an electrolyte (or separator) layer, and (3) a cathode layer, it would be difficult to reduce the size of the current collectors within the anode and cathode in this process.

Short circuits are also caused by misplacement or misalignment during

15 assembly. For example, in the placement of each component piece upon the underlying pieces, prior to lamination or welding, any misplacement, or skewing of the topmost piece can, later, result in shorting if a small portion of the edge of one electrode becomes positioned such that it can touch a portion of the opposite electrode, especially due to pressure, flexure or movement caused

20 by thermal expansion or contraction.

### SUMMARY OF THE INVENTION

The present invention is based in part on a process of fabricating electrochemical cells and batteries wherein the successive anode and cathode

25 layers are separated by a polymeric electrolyte layer having a protruding polymer edge or strip around its perimeter which reduces the likelihood of inadvertent contact between adjacent anode and cathode current collectors. The polymer edge functions as a non-conducting physical barrier.

In one aspect, the invention is directed to a method of preparing an electrochemical cell comprising the steps of:

- (a) forming an anode film onto at least one surface of an anode current collector to form an anode;
- 5 (b) forming a cathode film onto at least one surface of a cathode current collector to form a cathode; and
- (c) interposing a polymeric layer containing an electrolyte solution between the anode and cathode wherein the polymeric layer has a surface area that is larger than that of the anode film and cathode film, wherein the  
10 perimeter of the polymeric electrolyte layer forms an exposed strip that serves as a barrier to direct contact between the anode current collector and cathode current collector.

In another aspect, the invention is directed to a method of preparing an electrochemical cell comprising the steps of:

- 15 (a) preparing a polymeric layer comprising a first plasticizer;
- (b) covering at least one surface of an anode current collector with a layer of anode material comprising a first polymer, an intercalation carbon material, and a second plasticizer to form an anode precursor wherein each layer of said anode material has a surface area that is smaller than that of the  
20 polymeric layer;
- (c) covering at least one surface of a cathode current collector with a layer of cathode material comprising a second polymer, a cathode active material, and a third plasticizer to form a cathode precursor wherein each layer of said cathode material has a surface area that is smaller than that of the  
25 polymeric layer;
- (d) interposing the polymeric layer between the anode precursor and the cathode precursor so that the perimeter of the polymeric layer forms an exposed

strip that serves as a barrier to direct contact between the anode current collector and cathode current collector;

(e) removing said first, second, and third plasticizer; and

(f) placing an electrolyte solution comprising an electrolyte solvent and an inorganic salt into said anode precursor, cathode precursor, and polymeric layer.

In a further aspect, the invention is directed to an electrochemical cell comprising:

an anode having an anode current collector with an anode film on at least one side of the anode current collector;

a cathode having a cathode current collector with a cathode film on at least one side of the cathode current collector; and

a polymeric layer containing an electrolyte solution comprising an electrolyte solvent and a salt that is interposed between the anode and cathode, wherein the polymeric layer has a surface area that is larger than that of the anode film and cathode film, wherein the perimeter of the polymeric layer forms an exposed strip that serves as a barrier to direct contact between the anode current collector and cathode current collector.

In accordance with still another aspect of the present invention, an apparatus for preparing an electrochemical cell is provided. The apparatus includes a first laminating station, an anode current collector being laminated to at least one anode material film on at least one side of the anode current collector to form an anode precursor at the first laminating station, the anode current collector including an extending anode tab extending past an edge of the anode material film, and the anode material film including a first polymer, an intercalation carbon material, and a first plasticizer. The apparatus further includes a second laminating station, a cathode current collector being laminated to at least one cathode material film on at least one side of the cathode current

collector to form a cathode precursor at the second laminating station, the cathode current collector including an extending cathode tab extending past an edge of the cathode material film, and the cathode material film including a second polymer, a cathode active material, and a second plasticizer. The

5 apparatus further includes an assembling station, a polymeric layer including a third plasticizer being interposed between the anode precursor and the cathode precursor at the assembling station such that the polymeric layer prevents direct contact between the anode current collector and the cathode current collector. The apparatus further includes a fusion station, the polymeric layer being fused

10 to the anode precursor and the cathode precursor at the fusion station to form a bicell battery. The apparatus further includes a stacking station, a plurality of bicell batteries being stacked on top of one another at the stacking station to form a stack. The apparatus further includes a welding station, a plurality of anode tabs of the stack being welded to one another and to a conductive anode

15 lead, and a plurality of cathode tabs of the stack being welded to one another and to a conductive cathode lead at the welding station. The apparatus further includes an extraction station, downstream from the welding station, the first, second, and third plasticizers being extracted from the stack at the extraction station. The apparatus further includes an installation station, downstream from

20 the extraction station, the stack being installed in a recess in a stack receptacle such that at least portions of the anode lead and the cathode lead extend beyond an outer periphery of the stack receptacle. The apparatus further includes a filling station, an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into the receptacle and into the anode precursor, the

25 cathode precursor, and the polymeric layer at the filling station. The apparatus further includes a closing station, a top being closed over the recess in the stack receptacle such that the portions of the anode lead and the cathode lead are disposed outside of an outer periphery of the closed stack receptacle.

In accordance with still another aspect of the present invention, an apparatus for preparing an electrochemical cell is provided. The apparatus includes an assembling station, a polymeric layer including a first plasticizer being interposed between (a) an anode precursor, the anode precursor including  
5 an anode current collector laminated to at least one anode material film on at least one side of the anode current collector, the anode material film including a first polymer, an intercalation carbon material, and a second plasticizer, and (b) a cathode precursor, the cathode precursor including a cathode current collector laminated to at least one cathode material film on at least one side of the  
10 cathode current collector, the cathode material film including a second polymer, a cathode active material, and a third plasticizer, at the assembling station such that the polymeric layer prevents direct contact between the anode current collector and the cathode current collector. The apparatus further includes an extraction station, downstream from the assembling station, the first, second,  
15 and third plasticizers being extracted from the anode precursor, the cathode precursor, and the polymeric layer, respectively, at the extraction station. The apparatus further includes a filling station, an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into the anode precursor, the cathode precursor, and the polymeric layer at the filling station.

20 In accordance with another aspect of the invention, an apparatus for activating an electrochemical cell is described. The apparatus includes a first filling station, a first amount of an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into a receptacle for one or more bicell batteries such that the electrolyte solution is absorbed into pores in the  
25 anode precursor, the cathode precursor, and the polymeric layer of the one or more bicell batteries, from which first, second, and third plasticizers, respectively, have been extracted, at the first filling station. The apparatus further includes one or more subsequent filling stations disposed downstream



from the first filling station. Subsequent amounts of the electrolyte solution are filled into the receptacle at the subsequent filling stations such that the electrolyte solution is absorbed into pores in the anode precursor, the cathode precursor, and the polymeric layer at the subsequent filling stations. The subsequent amounts of the electrolyte solution added at each subsequent filling station is no more than equal to the amount added at a preceding one of the first filling station and the subsequent filling stations. The apparatus includes means for transporting the one or more bicell batteries disposed in the recess in the receptacle to and from the first filling station and to and from the one or more subsequent filling stations.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a schematic, cross-sectional view of an electrochemical cell;  
FIG. 2 is a schematic, top view of an electrochemical cell;  
FIG. 3 is a schematic view of an embodiment of an apparatus for preparing an electrochemical cell according to an embodiment of the present invention; and  
FIG. 4 is a schematic view of an embodiment of a filling or activation apparatus according to an embodiment of the present invention.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION**

The present invention is directed to a method of preparing electrochemical cells. Preferred cells include: a cathode comprising an active material, an intercalation based carbon anode, with each electrode capable of reversibly incorporating (e.g., intercalating) an alkali metal ion, and a polymeric matrix containing an electrolyte solution comprising an organic electrolyte solvent and a salt of the alkali metal. Each electrode has a current

collector. Particularly preferred electrochemical cells and batteries use lithium and salts thereof.

The anode of the present invention generally comprises an anode film that is laminated onto one or both sides of the current collector which is a thin metal foil or grid. Typically, each anode film is from about  
5 100  $\mu\text{m}$  to about 250  $\mu\text{m}$  in thickness, preferably about 110  $\mu\text{m}$  to about 200  $\mu\text{m}$ , and more preferably about 125  $\mu\text{m}$  to about 175  $\mu\text{m}$

Similarly, the cathode of the present invention generally comprises a cathode film that is laminated onto one or both sides of the cathode current  
10 collector which is a thin metal foil or grid. Typically, each cathode film is from about 100  $\mu\text{m}$  to about 200  $\mu\text{m}$  in thickness, preferably about 130  $\mu\text{m}$  to about 175  $\mu\text{m}$ , and more preferably about 140  $\mu\text{m}$  to about 165  $\mu\text{m}$ .

The anode and cathode each also includes a current collector that comprises, for example, a screen, grid, expanded metal, woven or non-woven  
15 or knitted wire fabric formed from an electron conductive material such as metals or alloys. Preferably, the current collector has a thickness from about 100  $\mu\text{m}$  to about 250  $\mu\text{m}$ , preferably about 110  $\mu\text{m}$  to about 200  $\mu\text{m}$ , and more preferably about 125  $\mu\text{m}$  to about 175  $\mu\text{m}$ . Each current collector is also connected to a current collector tab which extends from the edge of the current  
20 collector. In batteries comprising multiple electrochemical cells, the anode tabs are preferably welded together and connected to a lead. The cathode tabs are similarly welded and connected to a lead. External loads can be electrically connected to the leads. Current collectors and tabs are described in U.S. Patent 4,925,752, 5,011,501, and 5,326,653, which are incorporated  
25 herein.

However, prior to describing this invention in further detail, the following terms will be defined.

The term "plasticizer" refers to an organic solvent, with limited solubility of polymers, that facilitates the formation of porous polymeric structures. By "porous structure" is meant that upon extraction of the plasticizer the polymer remains as a porous mass. Suitable plasticizers have high boiling points typically from about 100°C to about 350°C. A number of criteria are important in the choice of plasticizer including compatibility with the components of the electrochemical cell precursor, processability, low polymer solubility and extractability liquid solvents (e.g., diethyl ether) or by dense gases for example. Preferred plasticizers include, for example, dibutyl phthalate, dioctylphthalate, and acetates, glymes, and low molecular weight polymers.

In operation, the plasticizer is first well mixed with a polymer. Thereafter the plasticizer is removed by extraction and in the process the porous structure is formed. Preferably the weight ratio of plasticizer to polymer is from about 1 to about 50, more preferably about 10 to about 30, and most preferably about 20 to about 25.

The term "electrochemical cell precursor" or "electrolytic cell precursor" refers to the structure of the electrochemical cell prior to the addition of the inorganic salt and electrolyte solvent. The precursor typically comprises (each in precursor form) an anode, a cathode, and polymeric matrix. The anode and/or cathode may each include a current collector. The polymeric matrix can function as a separator between the anode and cathode.

The term "activation" refers to the placement of an inorganic salt and electrolyte solvent into the porous portions of an electrochemical cell precursor. After activation, the electrochemical cell is charged by an external energy source prior to use.

The term "electrolytic cell" or "electrochemical cell" refers to a composite containing an anode, a cathode and polymeric layer comprising an electrolyte solution interposed therebetween.

5 The term "battery" refers to two or more electrochemical cells electrically interconnected in an appropriate series/parallel arrangement to provide the required operating voltage and current levels.

10 The term "solid polymeric matrix" refers to an electrolyte compatible material formed by polymerizing an inorganic or organic monomer (or partial polymer thereof) and which, when used in combination with the other components of the electrolyte, renders the electrolyte solid. Suitable solid polymeric matrices are well known in the art and include solid matrices formed from inorganic polymers, organic polymers or a mixture of organic polymers with inorganic non-polymeric materials. The solid polymeric matrix is an organic matrix derived from a solid matrix forming monomer and from partial  
15 polymers of a solid matrix forming monomer. See, for example, U.S. Patent 4,925,751, which is incorporated herein.

Alternatively, the solid polymeric matrix can be used in combination with a non-polymeric inorganic matrix. See, for example, U.S. Patent No. 4,990,413, which is incorporated herein by reference in its entirety. Suitable  
20 non-polymeric inorganic materials for use in conjunction with the solid polymeric matrix include, by way of example,  $\beta$ -alumina, silver oxide, lithium iodide, and the like. Suitable inorganic monomers are also disclosed in U.S. Patent Nos. 4,247,499, 4,388,385, 4,414,607, 4,394,280, 4,432,891, 4,539,276, and 4,557,985 each of which is incorporated herein by reference.

25 The term "a solid matrix forming monomer" refers to inorganic or organic materials which in monomeric form can be polymerized, preferably in the presence of an inorganic ion salt, and a solvent mixture of an organic carbonate and a glyme compound, to form solid matrices which are suitable for

use as solid electrolytes in electrolytic cells. Suitable solid matrix forming monomers are well known in the art and the particular monomer employed is not critical. The solid matrix forming monomers may also comprise hetero-atoms capable of forming donor acceptor bonds with inorganic cations (e.g.,  
5 alkali ions).

Examples of suitable organic solid matrix forming monomers include, by way of example, propylene oxide, ethyleneimine, ethylene oxide, epichlorohydrin, acryloyl-derivatized polyalkylene oxides (as disclosed in U.S. Patent No. 4,908,283), urethane acrylate, vinyl sulfonate polyalkylene oxides  
10 (as disclosed in U.S. Patent No. 5,262,253, which patent is incorporated herein by reference in its entirety), and the like as well as mixtures thereof. Examples of suitable inorganic solid matrix forming monomers include, by way of example, phosphazenes and siloxanes. Phosphazene monomers and the resulting polyphosphazene solid matrix are disclosed by Abraham et al., Proc.  
15 Int. Power Sources Symp., 34th, pp. 81-83 (1990) and by Abraham et al., J. Electrochemical Society, Vol. 138, No. 4, pp. 921-927 (1991).

The term "a partial polymer of a solid matrix forming monomer" refers to solid matrix forming monomers which have been partially polymerized to form reactive oligomers. Partial polymerization may be conducted for the  
20 purpose of enhancing the viscosity of the monomer, decreasing the volatility of the monomer, and the like. Partial polymerization is generally permitted so long as the resulting partial polymer can be further polymerized, preferably in the presence of a solvent, such as, a mixture of organic carbonate(s) to form solid polymeric matrices which are suitable for use as a polymeric layer in  
25 electrolytic cells.

The term "cured" or "cured product" refers to the treatment of the solid matrix forming monomer or partial polymer thereof under polymerization conditions (including cross-linking) so as to form a solid polymeric matrix.

Suitable polymerization conditions are well known in the art and include by way of example, heating the monomer, irradiating the monomer with UV light, electron beams, and the like. The resulting cured product preferably contains repeating units containing at least one heteroatom such as oxygen or nitrogen which is capable of forming donor acceptor bonds with inorganic cations (alkali ions). Examples of suitable cured products suitable for use in this invention are set forth in U.S. Patent Nos. 4,830,939 and 4,990,413 which are incorporated herein by reference in their entirety.

The solid matrix forming monomer or partial polymer can be cured or further cured prior to or after addition of the salt, solvent and, optionally, a viscosifier. For example, a composition comprising requisite amounts of the monomer or partial polymer, salt, organic carbonate solvent and viscosifier can be applied to a substrate and then cured. Alternatively, the monomer or partial polymer can be first cured and then dissolved in a suitable volatile solvent. Requisite amounts of the salt, organic carbonate solvent and viscosifier can then be added. The mixture is then placed on a substrate and cured; removal of the volatile solvent would result in the formation of a solid electrolyte. In either case, the resulting solid electrolyte would be a homogeneous, single phase product which is maintained upon curing, and does not readily separate upon cooling to temperatures below room temperature.

Alternatively, the solid polymeric matrix can be formed by a casting process which does not require the use of monomers or prepolymers, that is, no curing is required. A preferred method employs a copolymer of polyvinylidenedifluoride and hexafluoropropylene dissolved in acetone or other suitable solvent(s). Upon casting the solution, the solvent is evaporated to form the solid polymeric matrix. The solution may be casted directly onto a current collector. Alternatively, the solution is casted onto a substrate, such as a

carrier web, and after the solvent (e.g., acetone) is removed, an electrode film is formed thereon.

The term "salt" refers to any salt, for example, an inorganic salt, which is suitable for use in a non-aqueous electrolyte. Representative examples of suitable inorganic ion salts are alkali metal salts of less mobile anions of weak bases having a large anionic radius. Examples of such anions are  $I^-$ ,  $Br^-$ ,  $SCN^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $CF_3COO^-$ ,  $CF_3SO_3^-$ ,  $N(SO_2CF_3)_2^-$ , and the like. Specific examples of suitable inorganic ion salts include  $LiClO_4$ ,  $LiSCN$ ,  $LiBF_4$ ,  $LiAsF_6$ ,  $LiCF_3SO_3$ ,  $LiPF_6$ ,  $(CF_3SO_2)_2NLi$ ,  $(CF_3SO_2)_3CLi$ ,  $NaSCN$ , and the like. The inorganic ion salt preferably contains at least one cation selected from the group consisting of Li, Na, Cs, Rb, Ag, Cu, Mg and K.

The electrolyte typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably from about 10 to about 15 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed.

The term "compatible electrolyte solvent" or "electrolytic solvent," or in the context of components of the non-aqueous electrolyte, just "solvent," is a low molecular weight organic solvent added to the electrolyte and/or the cathode composition, which may also serve the purpose of solvating the inorganic ion salt. The solvent is any compatible, relatively non-volatile, aprotic, relatively polar, solvent. Preferably, these materials have boiling points greater than about 85°C to simplify manufacture and increase the shelf life of the electrolyte/battery. Typical examples of solvent are mixtures of such materials as dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, methyl ethyl carbonate, gamma-butyrolactone, triglyme, tetraglyme, dimethylsulfoxide, dioxolane, sulfolane, and the like. When using propylene carbonate based electrolytes in an electrolytic cell with graphite

anodes, a sequestering agent, such as a crown ether, is added in the electrolyte.

For electrochemical cells where (1) the cathode comprises lithiated cobalt oxides, lithiated manganese oxides, lithiated nickel oxides,  $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ , where x is preferably about 1 and y is preferably 0.1-0.9,  $\text{LiNiVO}_4$ , or  
 5  $\text{LiCoVO}_4$ , and (2) the anode comprises carbon, the electrolytic solvent preferably comprises a mixture of ethylene carbonate and dimethyl carbonate. For electrochemical cells where the cathode comprises vanadium oxides, e.g.,  $\text{V}_6\text{O}_{13}$  and the anode is lithium, the electrolytic solvent preferably comprises a mixture of propylene carbonate and triglyme.

10 The term "organic carbonate" refers to hydrocarbyl carbonate compounds of no more than about 12 carbon atoms and which do not contain any hydroxyl groups. Preferably, the organic carbonate is an aliphatic carbonate and more preferably a cyclic aliphatic carbonate.

Suitable cyclic aliphatic carbonates for use in this invention include  
 15 1,3-dioxolan-2-one (ethylene carbonate); 4-methyl-1,3-dioxolan-2-one (propylene carbonate); 4,5-dimethyl-1,3-dioxolan-2-one; 4-ethyl-1,3-dioxolan-2-one; 4,4-dimethyl-1,3-dioxolan-2-one; 4-methyl-5-ethyl-1,3-dioxolan-2-one; 4,5-diethyl-1,3-dioxolan-2-one; 4,4-diethyl-1,3-dioxolan-2-one; 1,3-dioxan-2-one; 4,4-dimethyl-1,3-dioxan-2-one; 5,5-dimethyl-  
 20 1,3-dioxan-2-one; 5-methyl-1,3-dioxan-2-one; 4-methyl-1,3-dioxan-2-one; 5,5-diethyl-1,3-dioxan-2-one; 4,6-dimethyl-1,3-dioxan-2-one; 4,4,6-trimethyl-1,3-dioxan-2-one; and spiro (1,3-oxa-2-cyclohexanone-5',5',1',3'-oxa-2'-cyclohexanone).

Several of these cyclic aliphatic carbonates are commercially available  
 25 such as propylene carbonate and ethylene carbonate. Alternatively, the cyclic aliphatic carbonates can be readily prepared by well known reactions. For example, reaction of phosgene with a suitable alkane- $\alpha,\beta$ -diol (dihydroxy



alkanes having hydroxyl substituents on adjacent carbon atoms) or an alkane- $\alpha,\gamma$ -diol (dihydroxy alkanes having hydroxyl substituents on carbon atoms in a 1,3 relationship) yields an a cyclic aliphatic carbonate for use within the scope of this invention. See, for instance, U.S. Patent No. 4,115,206,  
5 which is incorporated herein by reference in its entirety.

Likewise, the cyclic aliphatic carbonates useful for this invention may be prepared by transesterification of a suitable alkane- $\alpha,\beta$ -diol or an alkane- $\alpha,\gamma$ -diol with, e.g., diethyl carbonate under transesterification conditions. See, for instance, U.S. Patent Nos. 4,384,115 and 4,423,205 which are incorporated  
10 herein by reference in their entirety. Additional suitable cyclic aliphatic carbonates are disclosed in U.S. Patent No. 4,747,850 which is also incorporated herein by reference in its entirety.

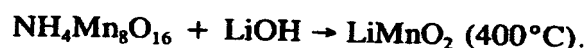
The term "viscosifier" refers to a suitable viscosifier for solid electrolytes. Viscosifiers include conventional viscosifiers such as those known  
15 to one of ordinary skill in the art. Suitable viscosifiers include film forming agents well known in the art which include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a number average molecular weight of at least about 100,000, polyvinylpyrrolidone, carboxymethylcellulose, and the like. Preferably, the viscosifier is employed in  
20 an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

The anode typically comprises a compatible anodic material which is any material which functions as an anode in a solid electrolytic cell. Such compatible anodic materials are well known in the art and include, by way of  
25 example, lithium, lithium alloys, such as alloys of lithium with aluminum, mercury, manganese, iron, zinc, intercalation based anodes such as those employing carbon, tungsten oxides, and the like. Preferred anodes include lithium intercalation anodes employing carbon materials such as graphite,

cokes, mesocarbons, and the like. Such carbon intercalation based anodes typically include a polymeric binder and extractable plasticizer suitable for forming a bound porous composite having a molecular weight of from about 1,000 to 5,000,000. Examples of suitable polymeric binders include EPDM (ethylene propylene diamine termonomer), PVDF (polyvinylidene difluoride), EAA (ethylene acrylic acid copolymer), EVA (ethylene vinyl acetate copolymer), EAA/EVA copolymers, and the like. The anode may also include an electron conducting material such as carbon black.

The cathode typically comprises a compatible cathodic material (i.e., insertion compounds) which is any material which functions as a positive pole in a solid electrolytic cell. Such compatible cathodic materials are well known in the art and include, by way of example, transition metal oxides, sulfides, and selenides, including lithiated compounds thereof. Representative materials include cobalt oxides, manganese oxides, molybdenum oxides, vanadium oxides, sulfides of titanium, molybdenum and niobium, the various chromium oxides, copper oxides, lithiated cobalt oxides, e.g.,  $\text{LiCoO}_2$  and  $\text{LiCoVO}_4$ , lithiated manganese oxides, e.g.,  $\text{LiMn}_2\text{O}_4$ , lithiated nickel oxides, e.g.,  $\text{LiNiO}_2$  and  $\text{LiNiVO}_4$ , and mixtures thereof. Cathode-active material blends of  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) are described in U.S. Patent 5,429,890 which is incorporated herein. The blends can include  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) and at least one lithiated metal oxide selected from  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  wherein  $0 < x \leq 2$ . Blends can also include  $\text{Li}_y\text{-}\alpha\text{-MnO}_2$  ( $0 \leq y < 1$ ) which is  $\text{Li}_y\text{NH}_4\text{Mn}_8\text{O}_{16}$  ( $0 \leq y < 1$ ) which has a hollandite-type structure. Blends comprising  $\text{Li}_y\text{-}\alpha\text{-MnO}_2$  where  $0 \leq y < 0.5$  are preferred.  $\alpha\text{MnO}_2$  can be synthesized by precipitation from a reaction between a  $\text{MnSO}_4$  solution and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidizing agent.

Lithiation (also referred to as "prelithiation") of  $\alpha\text{MnO}_2$  can be accomplished via a solid state reaction:



Li- $\alpha$ -MnO<sub>2</sub> retains the same structure as Hollandite. See, Botkovitz et. al., J. of Power Sources, 43-44 (1993) 657-665, which is incorporated herein, for a discussion of the structure and electrochemical characteristics of Li- $\alpha$ -MnO<sub>2</sub>. Li<sub>y</sub>- $\alpha$ -MnO<sub>2</sub> 0 ≤ y < 0.5 is commercially available from SEDEMA, Tertre, Belgium.

In one preferred embodiment, the compatible cathodic material is mixed with an electroconductive material including, by way of example, graphite, powdered carbon, powdered nickel, metal particles, conductive polymers (i.e., characterized by a conjugated network of double bonds like polypyrrole and polyacetylene), and the like, and a polymeric binder to form under pressure a positive cathodic plate. Suitable binders for use in the cathode have a molecular weight of from about 1,000 to 5,000,000.

In one preferred embodiment, the cathode is prepared from a cathode paste which comprises from about 35 to 65 weight percent of a compatible cathodic material; from about 1 to 20 weight percent of an electroconductive agent; from about 1 to 20 weight percent of suitable polymeric binders that may include EPDM (ethylene propylene diene termonomer), PVDF (polyvinylidene difluoride), EAA (ethylene acrylic acid copolymer), EVA (ethylene vinyl acetate copolymer), EAA/EVA copolymers, and the like; from about 0 to about 20 weight percent of polyethylene oxide having a number average molecular weight of at least 100,000; from about 10 to 50 weight percent of solvent comprising a 10:1 to 1:4 (w/w) mixture of an organic carbonate and a glyme; and from about 5 weight percent to about 25 weight percent of a solid matrix forming monomer or partial polymer thereof. Also included is an ion conducting amount of an inorganic ion salt. Generally, the amount of the salt is from about 1 to about 25 weight percent. (All weight percents are based on the total weight of the cathode.)

The electrolyte composition typically comprises from about 5 to about 25 weight percent of the inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably from about 10 to about 15 weight percent. The percentage of salt depends on the type of salt and electrolytic solvent employed.

The electrolyte composition typically comprises from 0 to about 80 weight percent electrolyte solvent (e.g., organic carbonate/glyme mixture) based on the total weight of the electrolyte; preferably from about 60 to about 80 weight percent; and even more preferably about 70 weight percent.

The electrolyte composition typically comprises from about 5 to about 30 weight percent of the solid polymeric matrix based on the total weight of the electrolyte; preferably from about 15 to about 25 weight percent.

In a preferred embodiment, the electrolyte composition further comprises a small amount of a film forming agent. Suitable film forming agents are well known in the art and include, by way of example, polyethylene oxide, polypropylene oxide, copolymers thereof, and the like, having a numbered average molecular weight of at least about 100,000. Preferably, the film forming agent is employed in an amount of about 1 to about 10 weight percent and more preferably at about 2.5 weight percent based on the total weight of the electrolyte composition.

#### Methodology

Electrochemical cells are known in the art. See, for example, U.S. Patents 5,300,373, 5,316,556, 5,346,385, 5,262,253, 4,472,487, 4,668,595, and 5,028,500, all of which are incorporated herein. The inventive method can be adapted to form anode, cathode, and/or polymeric matrix structures in prior art electrochemical cells. The following illustrates a method of how an electrolytic cell could be fabricated with the inventive process. Examples 1 and 2 describe the process of preparing the anode slurry and cathode slurry,

respectively. Example 3 describes the procedures for fabricating a solid electrolyte cell.

The invention will be described using the anode and cathode structures wherein electrode materials (or films) are laminated onto both sides of the current collectors, however, it is understood that the invention is applicable to other configurations, for example, where one side of the anode and/or cathode current collector is laminated.

### EXAMPLE 1

The anode current collector employed was a sheet of expanded copper metal that is about 50  $\mu\text{m}$  thick. It is available under the designation 2Cu5-125 (flatten) from Delker, in Branford, Connecticut.

The anode slurry was prepared as follows:

A polymer mixture comprising a copolymer of vinylidenedifluoride (VDF) and hexafluoropropylene (HFP) was prepared by mixing 6.8 grams of the copolymer in 20 grams of acetone. The copolymer (ave. MW 125K) was Kynar Flex 2801™ from Elf Atochem North America, in Philadelphia, Pennsylvania. The mixture was stirred for about 24 hours in a milling jar available from VWR Scientific, in San Francisco, California, model H-04172-00. The copolymer functions as a binder for the carbon in the anode.

A graphite mixture was prepared separately by first adding 23.4 grams of graphite into 0.9 grams of carbon black into a solution containing 60 grams acetone, 10.5 grams dibutyl phthalate, and 0.5 grams of a surfactant. A preferred graphite comprises a 50:50 (by weight) mixture of a synthetic graphite available under the designation SFG-15™ from Lonza G & T, Ltd. (Sins, Switzerland) and graphitized mesocarbon microbeads available under the designation MCMB25-28™ from Osaka Gas Co., Japan. A preferred carbon black is available under the designation Super P™ from M.M.M. Carbon,

Willebroek, Belgium. Preferred surfactants include Pluronic FC68™ from BASF, Mt. Olive, New Jersey and Flurad 430™ from 3M Co. St. Paul, Minnesota. The surfactant disperses the graphite. The graphite mixture was then vigorously mixed in a high shear mixer until a substantially homogeneous blend was formed. A suitable mixer is available from Ross Model ME100DLX, Hauppauge, New York, operating at its highest setting (about 10,000 RPM) for 30 minutes.

The anode slurry was prepared by mixing the polymer mixture and the graphite mixture together under low shear conditions to form the anode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it was laminated onto each side of the current collector. Anode films form when the remaining portion of the acetone evaporates.

## EXAMPLE 2

The cathode current collector employed was a sheet of expanded aluminum that is about 50  $\mu\text{m}$  thick. The aluminum grid is available under the designation 2AL5-077 from Delker, in Branford, Connecticut.

The cathode slurry was prepared as follows:

A polymer mixture comprising a copolymer of vinylidenedifluoride (VDF) and hexafluoropropylene (HFP) was prepared by mixing 4.4 grams of the copolymer in 15 ml of acetone. The copolymer was Kynar Flex 2801™. The mixture was stirred for about 24 hours in a milling jar.

A cathode mixture was prepared separately by first adding 28.9 grams of a cathode-active material blend comprising  $\text{Li}_x\text{Mn}_2\text{O}_4$  (spinel) ( $0 \leq x < 2$ ) and  $\text{Li}_{1-y}\alpha\text{-MnO}_2$  ( $0 \leq y < 1$ ) (1:1 weight ratio), 2.4 grams of carbon black (Super P™) into a solution containing 60 grams acetone, 8.7 grams dibutyl phthalate, and 0.5 grams of a surfactant. The mixture was then vigorously mixed in the a high shear mixer until a substantially homogeneous blend was formed.

The cathode slurry was prepared by mixing the polymer mixture and the graphite mixture together under low shear conditions to form the anode slurry wherein the components are well mixed. A portion of the acetone is allowed to evaporate from the slurry before it was laminated onto each side of the current collector. Cathode films form when the remaining portion of the acetone evaporates.

The above anode and cathode films were formed directly on the current collector by laminating the slurry mixtures onto the current collector surfaces. Alternatively, each film can be prepared by first casting a slurry onto a substrate or carrier web and allowing the solvent to evaporate thus leaving the film. Thereafter, the films can be laminated onto each side of the current collector.

### EXAMPLE 3

A solid electrochemical cell precursor is prepared by positioning a polymeric matrix between the anode and cathode and thereafter fusing the structures under moderate pressure and temperature (e.g., 130°C). The pressure and temperature employed will depend on the polymer(s) forming the matrix. The polymeric matrix is formed by casting a slurry comprising acetone, dibutyl phthalate, silanized fumed SiO<sub>2</sub>, and a VDF/HFP copolymer onto a carrier web or other substrate and allowing the acetone to evaporate. No curing by radiation is required. The SiO<sub>2</sub> is a filler which imparts toughness and strength to the film. In addition, it is believed that the SiO<sub>2</sub> assists the activation process by creating physico-chemical conditions such that the electrolyte solution quickly and completely fills the pores created by the extraction of the dibutyl phthalate. Preferably, the slurry is mixed under low shear conditions as not to degrade the copolymer. The anode, cathode, and separator films can be prepared separately or each can be fabricated in the form

of a long web and stored as individual rolls. Each web can be cut to size as needed.

As shown in figure 1, the precursor comprises an anode 10, a polymeric layer 20, and a cathode 30. The anode current collector 11 has a tab 12 protruding therefrom and the cathode collector 31 has a tab 32 protruding therefrom. The polymeric layer 20 has a surface area that is larger than that of the anode film and cathode film wherein the perimeter of the polymeric electrolyte layer forms an exposed strip that serves as a barrier to direct contact between the anode current collector and cathode current collector. Strip 21 preferably extends about 1-2.5mm from the edge of the precursor. Furthermore, preferably except for strip 21 and tabs 12 and 32, the side surface of the electrochemical cell precursor is continuous or flush. Each current collector tab is integral to the current collector. By integral is meant that the body of the current collector and tab form a unit, that is, they are not separate members that are attached (e.g., welded) together.

The anode components, namely the anode current collector and the anode films that are laminated on the top and lower surface of the current collector, preferably should have the same surface dimensions (e.g., same width and length). Similarly, the cathode components, namely the cathode current collector and the cathode films that are laminated on the top and lower surface of the current collector, preferably should have the same surface dimensions. The edge or perimeter of the current collectors are flush (i.e., aligned with) the edge of the electrode (anode and cathode) film. Although the surface geometry is not critical, it is also preferred that the anode and cathode surfaces have a regular configuration such as a rectangle or circle.

In fabricating a battery, a plurality of electrochemical precursors can be stacked one on top of each other so that the anode tabs line up on one side and the cathode tabs line up on the other. As shown in Figure 2, the anode tabs 50



are welded together and thereafter collectively electrically connected to a first nickel lead (not shown). Similarly, the cathode tabs 60 are welded together and thereafter collectively electrically connected to a second nickel lead (not shown). The leads are employed to connect to an external load. (Aluminum  
5 leads may also be used.)

Next the dibutyl phthalate is extracted from the precursor or plurality of electrochemical cell precursors in the case of a battery. Extraction can be accomplished using conventional organic liquid solvents such as diethyl ether or by a dense fluid or gas which refers to a gas compressed and heated to either  
10 supercritical or subcritical conditions to achieve liquid-like densities. Dense gases and fluids are known in the art. See, for example, U.S. Patents 5,013,366, 5,267,455, 4,219,333, 4,012,194, and 3,969,196, which are incorporated herein. A preferred dense gas is carbon dioxide.

Following extraction, the precursor is then packaged in moisture-  
15 impermeable material which is described, for example, in U.S. Patent 5,326,653 which is incorporated herein. The precursor is then activated. Extraction and activation are preferably done in an inert (e.g., argon) atmosphere. Finally, the packaging is sealed. Alternatively, the precursor (or plurality of electrochemical cell precursors) is pre-packaged in the moisture-  
20 impermeable material prior to extraction and activation.

An apparatus 101 for preparing an electrochemical cell according to an embodiment of the present invention is shown schematically in FIG. 3. The apparatus 101 preferably includes a first laminating station 103. At the first laminating station 103, an anode current collector 105 is laminated to at least  
25 one anode material film 107 on at least one side of the anode current collector, and, more preferably, is laminated to anode material film 107 on both sides of the anode current collector, to form an anode precursor 109. The anode current collector 105 preferably includes an extending anode tab 111 extending

past an edge 113 of the anode film, and the anode material film preferably includes, as discussed above, a first polymer, an intercalation carbon material, and a first plasticizer. The anode tab 111 may be provided by, for example, laminating the anode material film 107 over less than a complete width of the anode current collector 105. The first laminating station 103 preferably includes compressive elements such as nip rollers 115 for continuously laminating the anode current collector 105 to the anode material film or films 107, or compressive elements such as platens for intermittently laminating the anode current collector and the anode material film or films.

The apparatus 101 preferably includes a second laminating station 117, similar to the first laminating station 103. At the second laminating station 117, a cathode current collector 119 is preferably laminated to at least one cathode material film 121 on at least one side of the cathode current collector, and more preferably, is laminated to cathode material film on both sides of the cathode current collector, to form a cathode precursor 123. The cathode current collector 119 preferably includes an extending cathode tab 125 extending past an edge 127 of the cathode material film 121, and the cathode material film preferably includes a second polymer, a cathode active material, and a second plasticizer. The cathode tab 125 may be formed in the same manner as the anode tab 111. As with the first laminating station 103, nip rollers 129 or platens or other suitable compressive elements are preferably provided at the second laminating station 117 for laminating the cathode current collector 119 and the cathode material film 121.

A third laminating station 131, preferably identical to the second laminating station 117, is preferably also provided. At the third laminating station 131, a second cathode current collector 133 laminated to at least one second cathode material film 135 on at least one side of the second cathode current collector, and, more preferably, is laminated to cathode material film on

both sides of the second cathode current collector, to form a second cathode precursor 137. The second cathode precursor 137 is preferably the same as the first cathode precursor, such that the second cathode material film 135 includes the second polymer, the cathode active material, and the second plasticizer.

5 Like the first laminating station 103 and the second laminating station 117, the third laminating station 131 is preferably provided with suitable compressive elements such as nip rollers 139 or platens or the like.

The anode precursors 109, the cathode precursors 123, and, if provided, the second cathode precursors 137 may, if desired or necessary, be prepared at  
10 a site remote from the site at which the remaining steps in the assembly of the electrochemical cell. The apparatus 101 is described as including the first, second, and third laminating stations 103, 117, and 131 by way of example, not of necessity.

The apparatus 101 preferably includes an assembling station 141. At the  
15 assembling station 141, a polymeric layer 143 including a third plasticizer is interposed between the anode precursor 109 and the cathode precursor 123 such that the polymeric layer prevents direct contact between the anode current collector 105 and the cathode current collector 119. If a second cathode precursor 137 is provided, as is preferred, a second polymeric layer 145 is  
20 likewise interposed between the anode precursor 109 and the second cathode precursor, on a side of the anode precursor opposite the first cathode precursor 123.

At the assembling station 141, the anode precursor 109, the first polymeric layer 143, the cathode precursor 123, the second polymeric layer  
25 145, and the second cathode precursor 137 are preferably all sprayed, by one or more sprayers 147, with acetone or some other suitable material for softening the anode precursor, the first polymeric layer, the cathode precursor, the second polymeric layer, and the second cathode precursor sufficiently so that

those elements adhere to one another and are not easily displaced relative to one another. The assembly of the polymeric layer, the anode precursor 109, and the cathode precursor 123 and, if provided, the second polymeric layer 145 and the second cathode precursor 137 is preferably performed by a pick and place  
5 type of apparatus such as the one manufactured and sold by Klöckner Medipak, 14501 58th Street, Clearwater, Florida 34620. The anode precursor 109, the cathode precursor 123, and, if provided, the second cathode precursor 137, as well as the polymeric layer or layers, may be cut by a cutter 148 to a desired size corresponding to a desired amount of power desired from a battery to be  
10 formed from those components prior to joining the components, as is shown in FIG. 3, and subsequently sprayed with acetone, or may be first sprayed with acetone and joined, and then cut to size.

The apparatus 101 preferably includes a fusion station 149. At the fusion station 149, which is preferably part of the pick and place type apparatus  
15 described above, the polymeric layer 143 is fused, preferably under heat and pressure, to the anode precursor 109 and to the cathode precursor 123 to form a bicell battery 151. The bicell battery 151 includes the second cathode precursor 137 and the second polymeric layer 145, if those parts are provided. The fusion station 149 preferably includes a pair of platens 153 for compressing and  
20 heating the bicell battery 151 to cause the various layers thereof to fuse together. The platens 153 preferably pressurize the components of the bicell battery 151 that is preferably around 40 psi, and heat the components of the bicell battery to a temperature that is preferably around 110 °C - 160 °C.

The apparatus 101 preferably includes a stacking station 155, to which a  
25 plurality of bicell batteries 151 are moved by the pick and place machine after being fused at the fusion station and at which they are stacked on top of one another to form a stack 157. A presently preferred stack includes nine stacked bicells 151, each bicell including an anode precursor 109, a cathode precursor

123, and a second cathode precursor 137. The apparatus 101 preferably also includes a welding station 159 at which the plurality of anode tabs 111 of the stack 157 are welded to one another and also to a conductive anode lead 161, such as by an inductive welder 163, and at which a plurality of cathode tabs  
5 125 of the stack are welded to one another and also to a conductive cathode lead 165. The conductive anode lead 161 and the conductive cathode lead 165 add strength to the welded anode and cathode tabs which, alone, tend to have little strength, and the conductive anode and cathode leads are preferably formed of a conductive material such as nickel or copper.

10 The apparatus 101 further preferably includes an extraction station 167 to which the stack 157 is moved by the pick and place machine after welding at the welding station 159. At the extraction station 167, the first, second, and third plasticizers are extracted from the anode precursor, the cathode precursor and the second cathode precursor, if provided, and the polymeric layer or  
15 layers of the stack 157. The extraction of the plasticizers is preferably accomplished in the manner described above, e.g., preferably by using conventional organic solvents, such as diethyl ether or a dense fluid or gas.

The apparatus 101 preferably includes an installation station 169 to which the stack 157 is moved by the pick and place machine after extraction of the  
20 plasticizers at the extraction station 167. At the installation station 169, the stack 157 is preferably installed in a recess 171 in a stack receptacle 173 such that at least portions of the anode lead 161 and the cathode lead 165 extend beyond an outer periphery of the stack receptacle. These extending portions of the anode lead 161 and the cathode lead 165 form the external battery terminals  
25 in the completed battery. If desired or necessary, the apparatus 101 is provided with a stamping device 175 that forms the recess 171 in the stack receptacle 173, such as by stamping a flat sheet or web 177 of suitable material, such as

aluminum foil, to form the recess of suitable dimensions to receive the stack 157 therein.

5 The apparatus 101 preferably further includes a filling or activation station 179 to which the stack 157 and stack receptacle 173 are moved after the stack is placed in the recess 171 at the installation station 169. At the filling or activation station 179, an electrolyte solution including an electrolyte solvent and an inorganic salt are filled into the receptacle 173 and into the anode precursor, the cathode precursor, and the polymeric layer, from which the first, second, and third plasticizers have been extracted, thereby activating the  
10 resulting battery 181.

After the first, second, and third plasticizers have been extracted from the anode precursor 109, the cathode precursor 123, and the polymeric layer 143 to form pores therein, an electrolyte solution 201 must be added at the activation or filling station 179 to activate the stack 157, i.e., to make the stack into an  
15 actual battery 181. To avoid unnecessary repetition, the following description refers only to the cathode precursor 123 and its associated parts, and not to the second cathode precursor 137 and its associated parts, since the description of the following aspect of the present invention is identical for both the cathode precursor and the second cathode precursor.

20 According to a preferred embodiment of the present invention, as seen in FIG. 4, the activation station 179 includes a first filling station 203. A first amount of the electrolyte solution 201 is filled into the receptacle 173 such that the electrolyte solution is absorbed into the pores in the anode precursor, the cathode precursor, and the polymeric layer at the first filling station 203. One  
25 or more subsequent filling stations 205 are disposed downstream from the first filling station 203, and subsequent amounts of the electrolyte solution are filled into the receptacle 173 at the subsequent filling stations such that the electrolyte solution is absorbed into pores in the anode precursor, the cathode precursor,

and the polymeric layer at the subsequent filling stations. The electrolyte solution 201 is filled into the receptacle through conduits 207 through which flow may be controlled by any suitable means, such as by electronically controlled solenoid valves 209.

5       The subsequent amounts of the electrolyte solution 201 added at each subsequent filling station 205 is preferably no more than equal to the amount added at a preceding one of the first filling station 203 and the subsequent filling stations, since the anode precursor, the cathode precursor, and the polymeric layer tend to initially quickly absorb the electrolyte solution, and  
10       thereafter tend to more slowly absorb the electrolyte solution. For example, for a particular activation station, it is presently believed that it will be preferred to add more than half, actually, approximately 80% of the total electrolyte solution at the first filling station 203, 10% of the total electrolyte solution at the immediately subsequent filling station 205 after the first filling station, and  
15       5% of the total electrolyte solution at two more subsequent filling stations 205 to completely saturate the anode precursor, the cathode precursor, and the polymeric layer. However, the amounts added at the various filling stations will tend to be a function of factors such as the particular style and size of battery being activated, and other manufacturing constraints, and the foregoing  
20       example is not intended to be limiting. For example, since the anode current collector 105 of each anode precursor 109 is attached to an anode lead 161 and the cathode current collector 119 of each cathode precursor 123 is attached to a cathode lead 165, the first amount of electrolyte solution 201 filled at the first filling station 203 and the subsequent amounts of electrolyte solution filled at  
25       the one or more subsequent filling stations 205 is preferably small enough such that the electrolyte solution contacts neither the anode lead nor the cathode lead. In this way, problems associated with corrosion of the exposed portions of the anode lead 161 and the cathode lead 165 in the finished battery are minimized.

The one or more bicell batteries 151 forming the stack 157 disposed in the recess 171 in the receptacle 173 are transported to and from the first filling station 203 and to and from the one or more subsequent filling stations 205 by any suitable means, preferably in an intermittent fashion, such as by a pick and place type machine such as is noted above, or continuously, such as by a continuously moving conveyor belt. The length of time between filling at the first filling station 203 and filling at an immediately subsequent filling station 205 is preferably the same as a length of time between filling at any two successive subsequent filling stations. It is presently preferred to move the one or more bicell batteries 151 forming the stack 157 in the recess 171 in the receptacle 173 from the various filling stations 203 and 205 to an immediately subsequent filling station 205 every 2.5 seconds.

Preferably, the first amount of electrolyte solution 201 filled at the first filling station 203 and the subsequent amounts of electrolyte solution filled at the subsequent filling stations 205 is such that, and the length of time between filling at the first filling station and each of the subsequent filling stations is such that the first amount of electrolyte solution is completely absorbed into the pores in the anode precursor 109, the cathode precursor 123, and the polymeric layer 143 before any subsequent amount of electrolyte solution is filled at a subsequent filling station immediately subsequent to the first filling station. Similarly, for each subsequent filling station 205, any subsequent amount of electrolyte solution 201 is preferably completely absorbed into the pores in the anode precursor 109, the cathode precursor 123, and the polymeric layer 143 before any subsequent amount of electrolyte solution is filled at any immediately subsequent filling station.

As seen in FIG. 3, the apparatus 101 preferably further includes a sealing or closing station 183 at which a top 185 is closed over the recess 171 in the stack receptacle 173 such that the portions of the anode lead 161 and the



cathode lead 165 are disposed outside of an outer periphery of the closed stack receptacle.

While all of the foregoing components of the apparatus 101 have been described as being part of a single apparatus, it will be appreciated that the foregoing description is by way of example only, and that numerous discrete apparatus can be used to perform the various operations involved in preparing an electrochemical cell according to the present invention.

While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate the various modifications, substitutions, and changes which may be made without departing from the spirit hereof. The descriptions of the subject matter in this disclosure are illustrative of the invention and are not intended to be construed as limitations upon the scope of the invention.

**WHAT IS CLAIMED IS:**

1. A method of preparing an electrochemical cell comprising the steps of:
  - (a) forming an anode film onto at least one surface of an anode current collector to form an anode;
  - 5 (b) forming a cathode film onto at least one surface of a cathode current collector to form a cathode; and
  - (c) interposing a polymeric layer containing an electrolyte solution between the anode and cathode wherein the polymeric electrolyte layer has a surface area that is larger than that of the anode film and cathode film wherein  
10 the perimeter of the polymeric electrolyte layer forms an exposed strip that serves as a barrier to direct contact between the anode current collector and cathode current collector provided that either (i) in forming the anode an anode film is formed on both surfaces of the anode current collector, or (ii) in forming the cathode, a cathode film is formed on both surfaces of the cathode current collector, or (iii) and in forming the anode, an anode film is formed on  
15 both surfaces of the anode current collector and in forming the cathode a cathode film is formed on both surfaces of the cathode current collector.
2. The method of Claim 1 wherein said anode current collector has an anode film on each side and said cathode current collector has a cathode film on  
20 each side.
3. The method of Claim 1 wherein said anode current collector has a perimeter that is substantially flush with the perimeter of the anode film and the cathode current collector has a perimeter that is substantially flush with the perimeter of the cathode film.

4. The method of Claim 3 wherein said anode comprises an anode tab which is integral with said anode current collector and wherein said cathode comprises a cathode tab which is integral with said cathode current collector.

- 5           5. A method of preparing an electrochemical cell comprising the steps of:
- (a) preparing a polymeric layer comprising a first plasticizer;
  - (b) covering at least one surface of an anode current collector with a layer of anode material comprising a first polymer, an intercalation carbon material, and a second plasticizer to form an anode precursor wherein each layer of said  
10       anode material has a surface area that is smaller than that of the polymeric layer;
  - (c) covering at least one surface of a cathode current collector with a layer of cathode material comprising a second polymer, a cathode active material, and a third plasticizer to form a cathode precursor wherein each layer of said  
15       cathode material has a surface area that is smaller than that of the polymeric layer;
  - (d) interposing the polymeric layer between the anode precursor and the cathode precursor so that the perimeter of the polymeric layer forms an exposed strip that serves as a barrier to direct contact between the anode current  
20       collector and cathode current collector;
  - (e) removing said first, second, and third plasticizers; and
  - (f) placing an electrolyte solution comprising an electrolyte solvent and an inorganic salt into said anode precursor, cathode precursor, and polymeric layer provided that either (i) in forming the anode precursor a layer of anode material  
25       covers both surfaces of the anode current collector, or (ii) in forming the cathode precursor a layer of cathode material covers both surfaces of the cathode current collector, or (iii) in forming the anode precursor a layer of anode material covers both surfaces of the anode current collector and in

forming the cathode precursor a layer of cathode material covers both surfaces of the cathode current collector.

- 5       6. The method of Claim 5 wherein the anode material, cathode material, and polymeric layer each further comprises an inert liquid solvent and said method further comprises the step of removing said inert liquid solvents before step (f).
7. The method of Claim 5 wherein the first, second, and third plasticizers comprise dibutyl phthalate.
- 10      8. The method of Claim 6 wherein the inert liquid solvent comprises acetone.
9. The method of Claim 5 wherein said anode current collector has an anode film on each side and said cathode current collector has a cathode film on each side.
- 15      10. The method of Claim 5 wherein said anode current collector has a perimeter that is substantially flush with the perimeter of the anode film and the cathode current collector has a perimeter that is substantially flushed with the perimeter of the cathode film.
- 20      11. The method of Claim 10 wherein said anode comprises an anode tab which is integral with said anode current collector and wherein said cathode comprises a cathode tab which is integral with said cathode current collector.
12. An electrochemical cell comprising:

an anode layer having an anode current collector with an anode film on at least one side of the anode current collector;

a cathode layer having a cathode current collector with a cathode film on at least one side of the cathode current collector; and

- 5 a polymeric layer containing an electrolyte solution comprising an electrolyte solvent and a salt that is interposed between the anode and cathode, wherein the polymeric layer has a surface area that is larger than that of the anode film and cathode film, wherein the perimeter of polymeric electrolyte layer forms an exposed strip that serves as a barrier to direct contact between
- 10 the anode current collector and cathode current collector provided that either (i) both sides of the anode current collector are coated with an anode film, or (ii) both side of the cathode current collector are coated with a cathode film, or (iii) both sides of the anode current collector are coated with an anode film and both side of the cathode current collector are coated with a cathode film.

- 15 13. The electrochemical cell of Claim 12 wherein said anode current collector has an anode film on each side and said cathode current collector has a cathode film on each side.

- 20 14. The electrochemical cell of Claim 12 wherein said anode current collector has a perimeter that is substantially flush with the perimeter of the anode film and the cathode current collector has a perimeter that is substantially flush with the perimeter of the cathode film.

- 25 15. The electrochemical cell of Claim 14 wherein said anode comprises an anode tab which is integral with said anode current collector and wherein said cathode comprises a cathode tab which is integral with said cathode current collector.

16. The electrochemical cell of Claim 12, wherein the anode current collector comprises copper.
17. The electrochemical cell of Claim 12, wherein the cathode current collector comprises aluminum.
- 5 18. The electrochemical cell of Claim 12, wherein the anode film comprises carbon materials selected from the group consisting of graphite, cokes, and mesocarbons.
- 10 19. The electrochemical cell of Claim 12, wherein the cathode film comprises cathodic material selected from the group consisting of lithiated cobalt oxides, lithiated manganese oxides, lithiated nickel oxides, and mixtures thereof.
- 15 20. The electrochemical cell of Claim 18, wherein the cathode film comprises cathodic material selected from the group consisting of lithiated cobalt oxides, lithiated manganese oxides, lithiated nickel oxides, and mixtures thereof.
- 20 21. An apparatus for preparing an electrochemical cell, comprising:  
a first laminating station, an anode current collector being laminated to at least one anode material film on at least one side of the anode current collector to form an anode precursor at the first laminating station, the anode current collector including an extending anode tab extending past an edge of the anode material film, and the anode material film including a first polymer, an intercalation carbon material, and a first plasticizer;

a second laminating station, a cathode current collector being laminated to at least one cathode material film on at least one side of the cathode current collector to form a cathode precursor at the second laminating station, the cathode current collector including an extending cathode tab extending past an edge of the cathode material film, and the cathode material film including a  
5 second polymer, a cathode active material, and a second plasticizer;

an assembling station, a polymeric layer including a third plasticizer being interposed between the anode precursor and the cathode precursor at the assembling station such that the polymeric layer prevents direct contact between the anode current collector and the cathode current collector;  
10

a fusion station, the polymeric layer being fused to the anode precursor and the cathode precursor at the fusion station to form a bicell battery;

a stacking station, a plurality of bicell batteries being stacked on top of one another at the stacking station to form a stack;

15 a welding station, a plurality of anode tabs of the stack being welded to one another and to a conductive anode lead, and a plurality of cathode tabs of the stack being welded to one another and to a conductive cathode lead at the welding station;

20 an extraction station, downstream from the welding station, the first, second, and third plasticizers being extracted from the stack at the extraction station;

25 an installation station, downstream from the extraction station, the stack being installed in a recess in a stack receptacle such that at least portions of the anode lead and the cathode lead extend beyond an outer periphery of the stack receptacle;

a filling station, an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into the receptacle and into the anode precursor, the cathode precursor, and the polymeric layer at the filling station;

a closing station, a top being closed over the recess in the stack receptacle such that the portions of the anode lead and the cathode lead are disposed outside of an outer periphery of the closed stack receptacle.

22. The apparatus as set forth in claim 21, wherein the anode material  
5 film is laminated to both sides of the anode current collector at the first laminating station.

23. The apparatus as set forth in claim 21, wherein the cathode material film is laminated to both sides of the cathode current collector at the second laminating station.

10 24. The apparatus as set forth in claim 21, further comprising a third laminating station, a second cathode current collector being laminated to at least one second cathode material film on at least one side of the second cathode current collector to form a second cathode precursor at the second laminating station, the second cathode precursor being substantially the same as the first  
15 cathode precursor, and the second cathode material film including the second polymer, the cathode active material, and the second plasticizer, wherein, at the assembling station, a second polymeric layer including the third plasticizer is interposed between the anode precursor and the second cathode precursor such that the polymeric layer prevents direct contact between the anode current  
20 collector and the second cathode current collector, and, at the fusion station, the polymeric layer is fused to the anode precursor and the second cathode precursor to form the bicell battery.

25. An apparatus for preparing an electrochemical cell, comprising:



an assembling station, a polymeric layer including a first plasticizer being interposed between (a) an anode precursor, the anode precursor including an anode current collector laminated to at least one anode material film on at least one side of the anode current collector, the anode material film including a first  
5 polymer, an intercalation carbon material, and a second plasticizer, and (b) a cathode precursor, the cathode precursor including a cathode current collector laminated to at least one cathode material film on at least one side of the cathode current collector, the cathode material film including a second polymer, a cathode active material, and a third plasticizer, at the assembling station such  
10 that the polymeric layer prevents direct contact between the anode current collector and the cathode current collector;

an extraction station, downstream from the assembling station, the first, second, and third plasticizers being extracted from the anode precursor, the cathode precursor, and the polymeric layer, respectively, at the extraction  
15 station; and

a filling station, an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into the anode precursor, the cathode precursor, and the polymeric layer at the filling station.

26. The apparatus as set forth in claim 25, further comprising a fusion  
20 station, the polymeric layer being fused to the anode precursor and the cathode precursor at the fusion station to form a bicell battery.

27. The apparatus as set forth in claim 26, further comprising a stacking station, a plurality of bicell batteries being stacked on top of one another at the stacking station to form a stack.

28. The apparatus as set forth in claim 27, wherein the anode current collector includes an anode tab extending beyond an edge of the anode material film, and the cathode current collector includes a cathode tab extending beyond an edge of the cathode material film, the apparatus further comprising a welding station, a plurality of anode tabs of the stack being welded to one another and to a conductive anode lead, and a plurality of cathode tabs of the stack being welded to one another and to a conductive cathode lead at the welding station.

29. The apparatus as set forth in claim 28, further comprising an installation station, downstream from the extraction station, the stack being installed in a recess in a stack receptacle such that at least portions of the anode lead and the cathode lead extend beyond an outer periphery of the stack receptacle.

30. The apparatus as set forth in claim 29, further comprising a closing station, a top being closed over the recess in the stack receptacle such that the portions of the anode lead and the cathode lead are disposed outside of an outer periphery of the closed stack receptacle.

31. The apparatus as set forth in claim 27, further comprising an installation station, downstream from the extraction station, the stack being installed in a recess in a stack receptacle at the installation station.

32. The apparatus as set forth in claim 25, wherein, at the assembling station, a second polymeric layer including the third plasticizer is interposed between the anode precursor and a second cathode precursor, the second cathode precursor including a second cathode current collector laminated to at

least one second cathode material film on at least one side of the second cathode current collector, the second cathode precursor being substantially the same as the first cathode precursor, and the second cathode material film including the second polymer, the cathode active material, and the second plasticizer, such that the polymeric layer prevents direct contact between the anode current collector and the second cathode current collector, and, at the fusion station, the polymeric layer is fused to the anode precursor and the second cathode precursor to form the bicell battery.

33. The apparatus as set forth in claim 32, further comprising first, second, and third laminating stations, the anode material film and the anode current collector being laminated together at the first laminating station, the first cathode material film and the first cathode current collector being laminated together at the second laminating station, and the second cathode material film and the second cathode current collector being laminated together at the third laminating station.

34. The apparatus as set forth in claim 33, wherein, at the first laminating station, the anode material film is laminated to both sides of the anode current collector.

35. The apparatus as set forth in claim 33, wherein, at the second laminating station, the first cathode material film is laminated to both sides of the first cathode current collector, and, at the third laminating station, the second cathode material film is laminated to both sides of the second cathode current collector.

36. An apparatus for activating an electrochemical cell, the electrochemical cell including one or more bicell batteries disposed in a recess in a receptacle, the bicell battery including an anode precursor, the anode precursor including an anode current collector laminated to at least one anode material film on at least one side of the anode current collector, the anode material film including a first polymer, an intercalation carbon material, and a first plasticizer, a cathode precursor, the cathode precursor including a cathode current collector laminated to at least one cathode material film on at least one side of the cathode current collector, the cathode material film including a second polymer, a cathode active material, and a second plasticizer, and a polymeric layer including a third plasticizer being interposed between the anode precursor and the cathode precursor at the assembling station such that the polymeric layer prevents direct contact between the anode current collector and the cathode current collector, the polymeric layer being fused between the anode precursor and the cathode precursor, the first, second, and third plasticizers having been extracted from the anode precursor, the cathode precursor, and the polymeric layer to form pores therein, comprising:
- a first filling station, a first amount of an electrolyte solution including an electrolyte solvent and an inorganic salt being filled into the receptacle such that the electrolyte solution is absorbed into pores in the anode precursor, the cathode precursor, and the polymeric layer at the first filling station;
  - one or more subsequent filling stations disposed downstream from the first filling station, subsequent amounts of the electrolyte solution being filled into the receptacle at the subsequent filling stations such that the electrolyte solution is absorbed into pores in the anode precursor, the cathode precursor, and the polymeric layer at the subsequent filling stations, the subsequent amounts of the electrolyte solution added at each subsequent filling station being no more than

equal to the amount added at a preceding one of the first filling station and the subsequent filling stations; and

means for transporting the one or more bicell batteries disposed in the recess in the receptacle to and from the first filling station and to and from the one or more subsequent filling stations.

37. The apparatus as set forth in claim 36, wherein the anode current collector of each anode precursor is attached to an anode lead and the cathode current collector of each cathode precursor is attached to a cathode lead, the first amount of electrolyte solution filled at the first filling station and the subsequent amounts of electrolyte solution filled at the one or more subsequent filling stations being small enough such that the electrolyte solution contacts neither the anode lead nor the cathode lead.

38. The apparatus as set forth in claim 36, wherein the first amount of electrolyte solution filled at the first filling station and the subsequent amounts of electrolyte solution filled at the subsequent filling stations is such that, and a length of time between filling at the first filling station and each of the subsequent filling stations is such that the first amount of electrolyte solution is completely absorbed into the pores in the anode precursor, the cathode precursor, and the polymeric layer before any subsequent amount of electrolyte solution is filled at a subsequent filling station immediately subsequent to the first filling station and, for each subsequent filling station, any subsequent amount of electrolyte solution is completely absorbed into the pores in the anode precursor, the cathode precursor, and the polymeric layer before any subsequent amount of electrolyte solution is filled at any immediately subsequent filling station.

39. The apparatus as set forth in claim 36, wherein the transporting means includes an intermittently movable conveyor device.
40. The apparatus as set forth in claim 36, wherein the transporting means includes a continuously moving conveyor device.
- 5        41. The apparatus as set forth in claim 36, wherein a length of time between filling at the first filling station and filling at an immediately subsequent filling station is the same as a length of time between filling at any two successive subsequent filling stations.
- 10       42. The apparatus as set forth in claim 36, wherein more than half of a total amount of electrolyte solution filled at the first filling station and at all of the subsequent filling stations is filled at the first filling station.

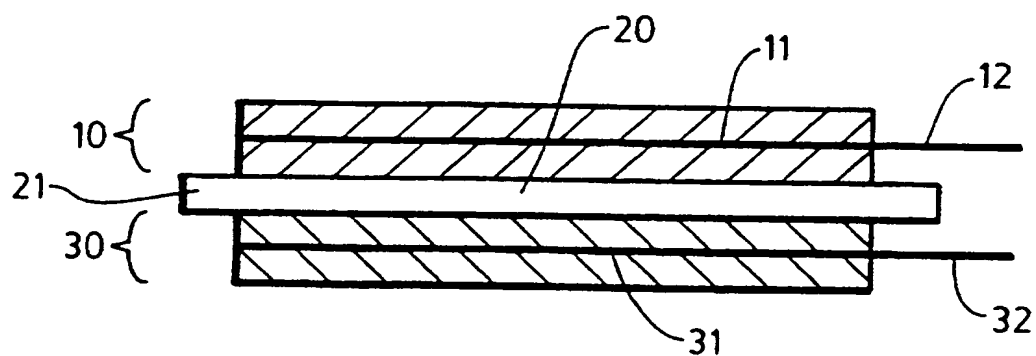


FIG. 1.

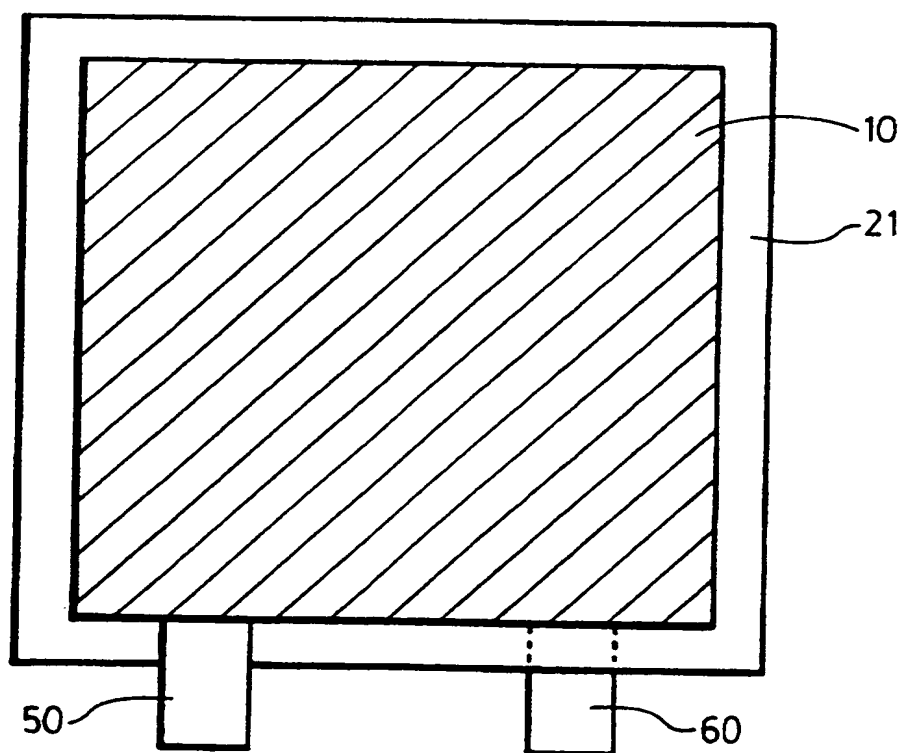


FIG. 2.

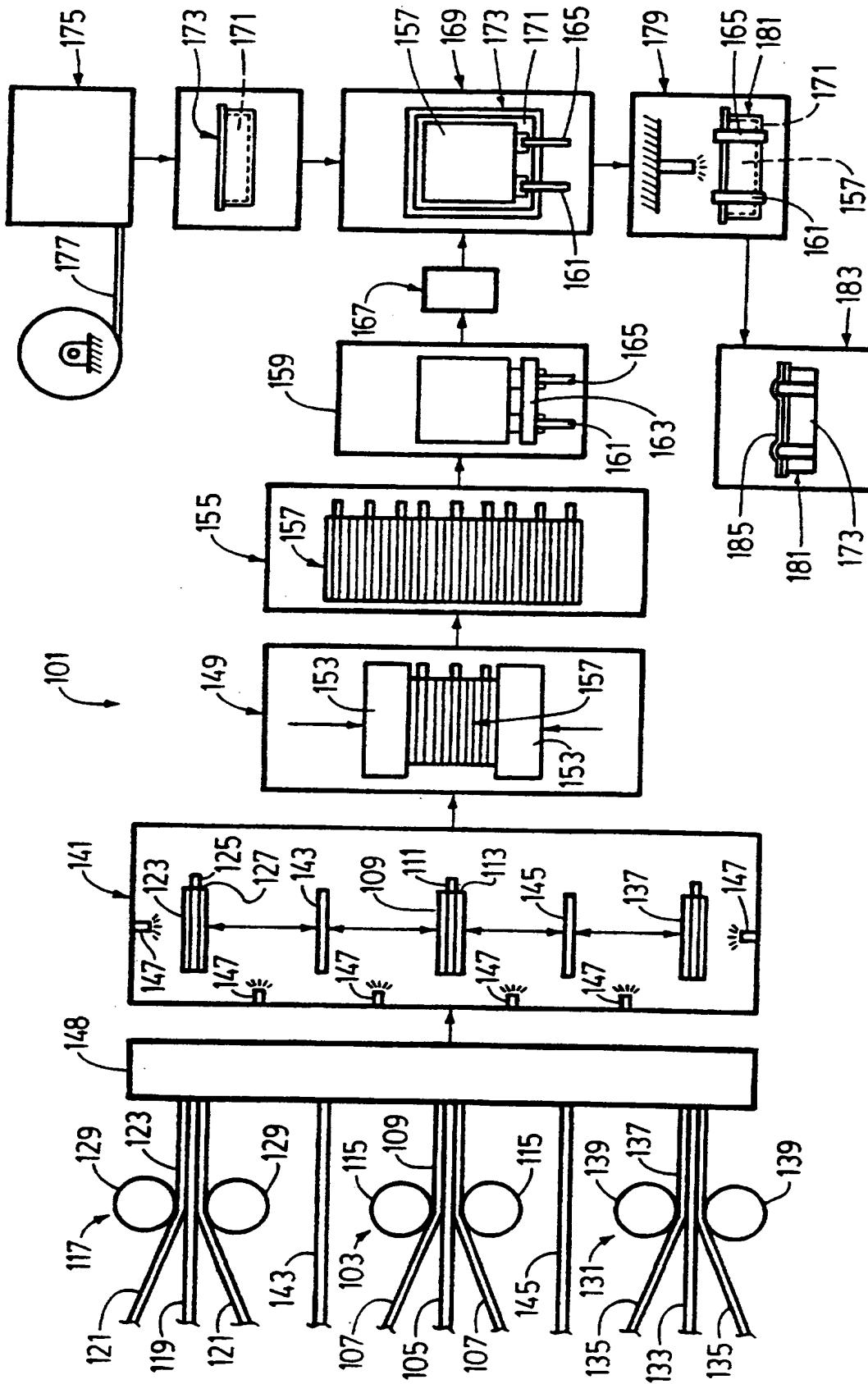


FIG. 3.



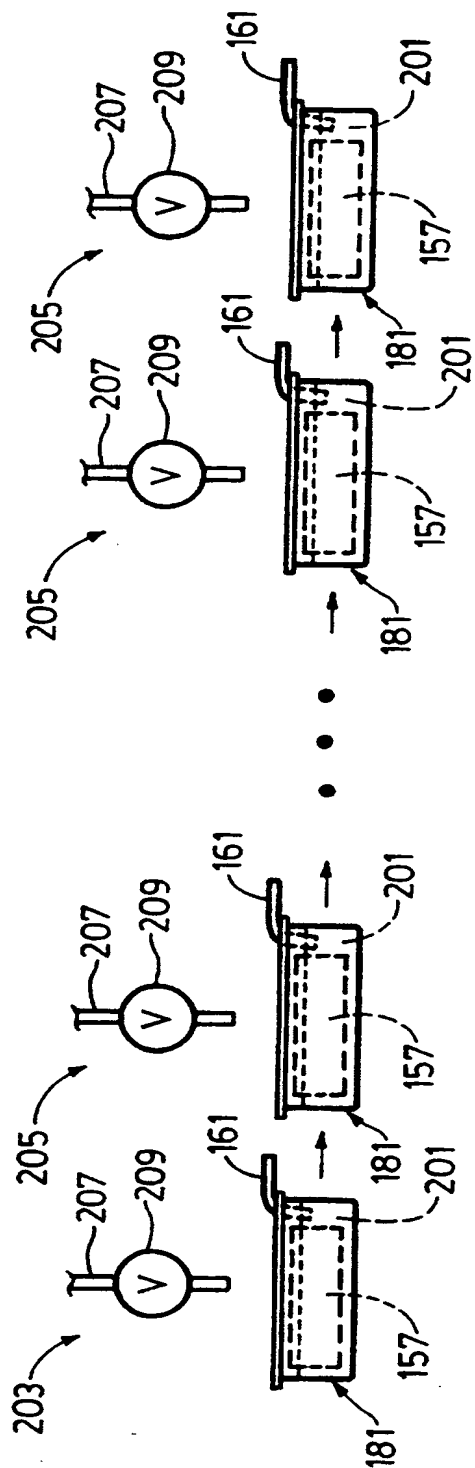


FIG. 4.

# 1

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/02305

### A. CLASSIFICATION OF SUBJECT MATTER

IPC6: H01M 10/04, H01M 6/46

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5460904 A (ANTONI S. GOZDZ ET AL), 24 October 1995 (24.10.95), column 3, line 11 - line 65 --	1, 12, 21, 25, 36
A	WO 9603781 A1 (MOTOROLA INC.), 8 February 1996 (08.02.96), page 4, line 21 - page 5, line 9, figure 1 --	1, 12, 21, 25, 36
A, P	US 5587253 A (ANTONI S. GOZDZ ET AL), 24 December 1996 (24.12.96), column 3, line 40 - column 4, line 32 --	1, 12, 21, 25, 36

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

10. 07. 97

Name and mailing address of the ISA/



European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 cpo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

ULLA GRANLUND

2

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US 97/02305

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A, E	WO 9708769 A1 (VALENCE TECHNOLOGY, INC.), 6 March 1997 (06.03.97), page 5, line 7 - line 28  -----	1, 12, 21, 25, 36

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

20/05/97

International application No.  
PCT/US 97/02305

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	5587253	A	24/12/96	AU	6457196 A	05/03/97
				IL	118907 D	00/00/00
				WO	9706569 A	20/02/97
				CA	2177361 A	08/06/95
				DE	737369 T	13/02/97
				EP	0737369 A	16/10/96
				IL	111559 D	00/00/00
				JP	9500485 T	14/01/97
				US	5456000 A	10/10/95
				US	5460904 A	24/10/95
				US	5470357 A	28/11/95
				US	5478668 A	26/12/95
				US	5540741 A	30/07/96
				US	5571634 A	05/11/96
				WO	9515589 A	08/06/95
				CA	2168433 A	02/03/95
				DE	714561 T	24/10/96
				EP	0714561 A	05/06/96
				JP	8509100 T	24/09/96
				US	5418091 A	23/05/95
				US	5429891 A	04/07/95
				US	5607485 A	04/03/97
				WO	9506332 A	02/03/95
				CA	2157012 A	15/09/94
				EP	0699348 A	06/03/96
				JP	8507407 T	06/08/96
				US	5296318 A	22/03/94
				WO	9420996 A	15/09/94
<hr/>						
WO	9708769	A1	06/03/97	NONE		
<hr/>						